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Growth of hematite and boehmite in concretions from ancient karst bauxite: clue for past climate

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Abstract

In the Peri-Adriatic Apulia Carbonate Platform (southern Italy), late Cretaceous karst bauxites mark an emergence period during a wet tropical climate. Bauxite formed through clay accumulation in the karst, “in situ” bauxitization and late formation of iron-rich concretions in a water-unsaturated pedogenic environment. The concretions, which are geochemical recorders of the environment of formation, have a large core of Al-hematite surrounded by a cortex of alternating Al-hematite and boehmite. Boehmite forms instead of Al-hematite at lower water activity values. Using a model of molecular diffusion and assuming the fluid flow negligible, the time necessary for growth of the concretions has been calculated. The average-sized core grew in ~ 180 ka. The Al-hematite accretionary band grew in ~ 8 ka whereas the boehmite accretionary band grew in ~ 4.5 ka. The average bulk concretions possibly formed in 300–400 ka. The growth of the concretions is assumed to be a two-stage process. In the first stage, the core grew in a relatively long period of wet tropical climate. In the second stage, drier conditions favouring boehmite stability alternated to a wetter climate favouring Al-hematite stability. The growth of the bulk concretions is consistent with the Earth’s long eccentricity cycle.

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Keywords: Late Cretaceous; Karst bauxites; Aluminium- and iron-rich concretions; Crystal growth; Climatic changes

1. Introduction

In the Mediterranean area, ancient karst bauxites, which are retained as markers of regional events, are widely spread (Bárdossy, 1982), and in the southern Apennines, they

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mark a Late Cretaceous period of emergence of the Peri-Adriatic Carbonate Platforms during a period of wet tropical climate (D'Argenio and Mindszenty, 1995). This platform drowning coincide with the tectonic rearrangement, from extensional to compressional, of part of the Tethyan region (Eberli, 1991). In the Apulia Carbonate Platform, the bauxite, filling karst depressions with steep and deep walls, occurred in a Neocomian–late Cenomanian limestone. The formation of these vertically developed cavities was favoured by a Cenomanian tectonic stage that, during the platform emergence stage (less than 3 Ma, Turonian–Santonian, D'Argenio and Mindszenty, 1995), originated a system of faults.

The bauxites, red in colour, were collected in the Spinazzola area (Fig. 1), and are formed by a fine-grained kaolinite-rich matrix which embeds iron-rich spheroidal concretions (Mongelli, 1997). The genetic model of formation involves accumulation of clay material in the karst, “in situ” bauxitization at the expense of the clay and late formation of the concretions in a pedogenic environment (Mongelli, 1997; Mongelli and Acquafredda, 1999). The pedogenic model is also in agreement with the isotopic signature ($\delta^{18}\text{O}$) of ancient oolitic ironstones from different sites and age which are all formed in

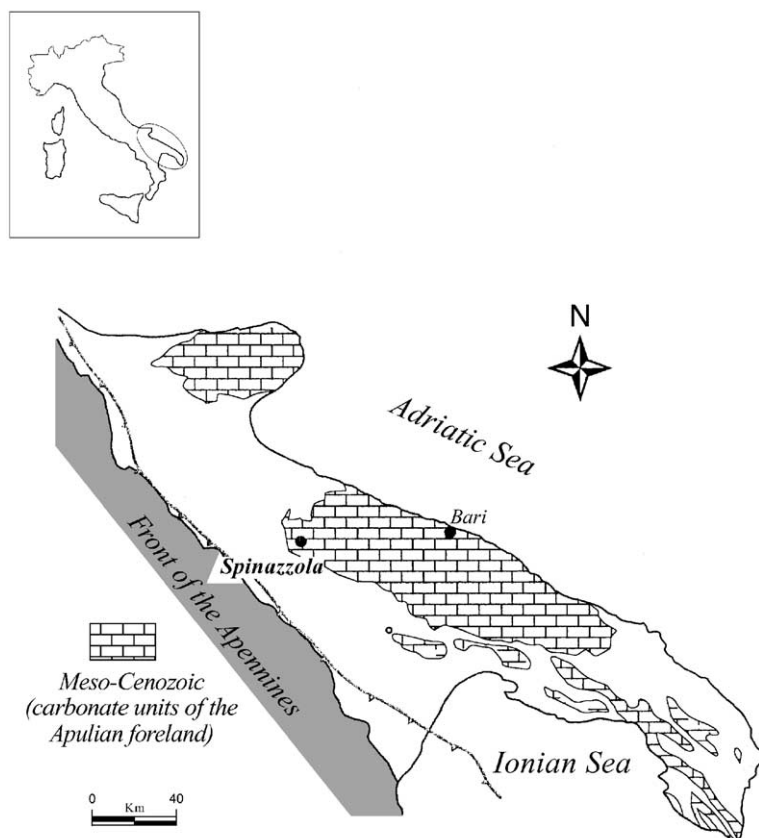


Fig. 1. Geological sketch map of the Apulian area including the location of the Spinazzola site.

continental settings (Yapp, 1998). The concretions have a well developed core, formed of Al-hematite, and a banded cortex of alternating Al-hematite and boehmite. Al-hematite and boehmite alternate in response to the environment of formation and boehmite may form instead of Al-hematite at high values of the $a_{\text{Al}^{3+}}/a_{\text{H}^{3+}}$ ratio coupled with lower values of water activity (Mongelli and Acquafredda, 1999).

In a tropical climate, the growth of ferruginous concretions, geochemical recorders of the changes in the environment in which they were formed, is a chemical transport-controlled phenomenon, mostly involving replacement at the expense of kaolinite (e.g. Bourrié and Pédro, 1979; Didier et al., 1983; Tardy and Nahon, 1985; Nahon, 1991). The goal of this study is to calculate the time necessary for growth of the concretions, using a model of molecular diffusion and assuming the fluid flow to be negligible (e.g. Frank, 1950; Berner, 1980), to verify if this time is consistent with the duration of the platform emergence stage and, further, if during this time palaeoenvironmental changes occurred.

2. The concretions

Ferruginous concretions are often observed in soils and alterites (e.g. Nahon, 1991) and their occurrence is related to iron migration toward pores of smaller size. In these soils and alterites, the concretions are formed of Al-hematite which replaces kaolinite through an epigenetic relation (Tardy and Nahon, 1985), although more recently, Tardy (1997) suggested that kaolinite and hematite coexist in an “amorphous” almost phase and boehmite forms by desilication and dehydration together with rings or cores of hematite. The Al-hematite can be considered as a member of the solid solution series between hematite and corundum. The molar fraction of Al_2O_3 is controlled by, among other factors, the water activity (Tardy and Nahon, 1985), thus, reflecting the water unsaturation of the system.

In the apulian karst bauxites from the Spinazzola site, the spheroidal concretions are well-shaped, equal in size, closely spaced and uniformly distributed in the bulk rock. Broken cortices and even broken nuclei are not observed, and radially or concentrically arranged fissures penetrating the concretions are rarely detected. This obviously excludes the occurrence of a second generation of concretions, formed through erosion at the expense of “in situ” formed first generation concretions (Delvigne, 1998). The concretions (Fig. 2) contain 55–75 wt.% of Fe_2O_3 and have a well-developed core, quite homogeneous in composition, and formed by aluminous hematite having $(\text{Al}_{0.12}\text{Fe}_{0.88})_2\text{O}_3$ as average representative formula (Mongelli, 1997; Mongelli and Acquafredda, 1999). The Al substitution is within the range of values observed in hematite formed through in situ epigenetic replacement of kaolinite, and involves a water unsaturated pedogenic environment (Mongelli and Acquafredda, 1999).

Microscopic observations carried out using a Cambridge S 360 scanning electron microscope and performed on well formed and unfissured concretions show that the core has an average radius of 34.1 μm ($n=25$, S.D.=12.4). The cortex surrounding the core is regular and is formed by alternating Al-hematite and boehmite layers (Mongelli, 1997). It is not possible to calculate the structural formula of Al-hematite

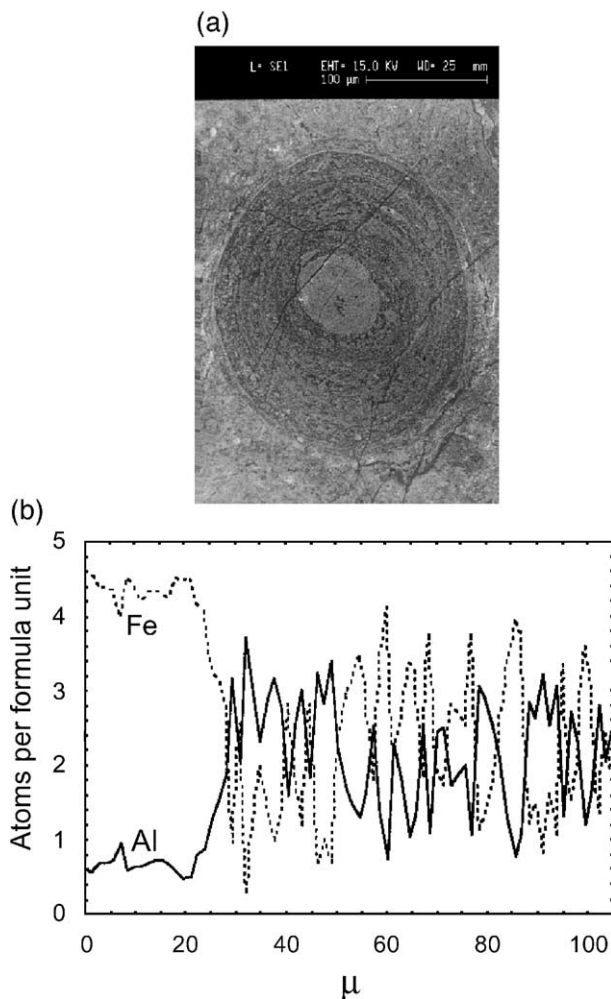


Fig. 2. (a) SEM microphotograph of a selected ooid formed by an Al-hematic core and a banded cortex of Al-hematite and boehmite. (b) Iron and aluminum distribution, obtained by EDX analysis, along a core-rim traverse in the SEM image.

and boehmite by the energy dispersive X-ray spectrometer coupled to the SEM because of the very narrow thickness of single accretionary bands (Al-hematite: average radius = $5.4\ \mu\text{m}$, $n = 137$, S.D. = 2.3; boehmite: average radius = $5.1\ \mu\text{m}$, $n = 144$, S.D. = 2.1), and considering that a single crystallite cannot be larger than the relative band. However, the maximum Al content observed in some bands is about four atoms per formula unit, whereas the Fe-content may reach the same levels as in the core (Mongelli and Acquafredda, 1999). Boehmite may form instead of Al-hematite at lower water activity values and its stability increases for high values of the $a_{\text{Al}^{3+}}/a_{\text{H}^{3+}}$ ratio. At neutral pH, the dominant dissolved Al species will be the hydrolyzed

form $\text{Al}(\text{OH})_4^-$. The $a_{\text{Al}^{3+}}/a_{\text{H}^+}^{3+}$ ratio is related to the hydroxy complex by the following (e.g. Wesolowski and Palmer, 1994):

$$\frac{a_{\text{Al}^{3+}}}{a_{\text{H}^+}^3} = K a_{\text{Al}(\text{OH})_4^-} a_{\text{H}^+} \quad (1)$$

and assuming the concentration of $\text{Al}(\text{OH})_4^-$ is approximately constant the $a_{\text{Al}^{3+}}/a_{\text{H}^+}^{3+}$ ratio and, in turn, the boehmite stability decreases with increasing pH. Boehmite formation in the concretions may be also favoured by conditions promoting the hematite instability including local reducing conditions, adsorption of ligands and an increase in the ionic strength (Biber et al., 1994).

3. Growth of concretions

In a stationary medium, the molecular diffusion is proportional to the concentration gradient and the movement is described by Fick's first law (in one dimension):

$$J = -D \left(\frac{dC}{dx} \right) \quad (2)$$

where J is the mass moving across a unit area in unit time and D is the diffusion coefficient. If dissolution of a preexisting mineral and simultaneous precipitation of a new mineral are both transport controlled and the fluid flow is negligible, the diffusion controlled growth of a sphere occurs. During this process, a zone of depletion develops around each growing crystal and Fick's first law is given by (e.g. Berner, 1980):

$$J_p = -\frac{\phi D}{L} (c_d - c_p) \quad (3)$$

where J_p is the mass moving across a unit area in unit time at the surface of the sphere, ϕ is the porosity, c is the molar equilibrium concentration in the pore water at outer surface of the zone of depletion (c_d) or at the surface of the sphere (c_p) and L is the thickness of the zone of depletion. According to Berner (1980), the time necessary to grow a spherical concretion having radius r_p is as follows:

$$t = \frac{r_p^2 (v_d F_p - v_p F_d) F_p^2}{2 \phi v_p^2 D (c_d - c_p) F_d F_p} \quad (4)$$

where v_p and F_p are the molar volume and the volume fraction of the precipitating mineral in the concretion, respectively. Similarly, v_d and F_d are the molar volume and the volume fraction in the bulk sediment of the dissolved mineral.

I assume that both hematite and boehmite are precipitating minerals growing at the expense of kaolinite. The molar volume of kaolinite is 99.31 cm^3 (Wedepohl, 1969) and that of boehmite is 19.535 cm^3 (Weast et al., 1986). Considering the effect of Al

substitution and assuming the possible incorporation of OH^- groups into the structure negligible, the molar volume of Al-hematite is calculated as follows (Stanjek and Schwertmann, 1992):

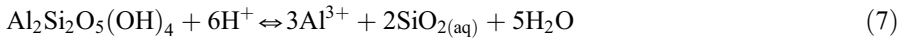
$$V = 0.318 - 0.0512\text{Al}/(\text{Fe} + \text{Al}) \quad (5)$$

Thus, for a molar substitution of 0.12 the molar volume of Al-hematite is 29.566 cm^3 . The matrix in which the concretions formed was probably very similar to the “terra rossa” presently observed on the limestone of the Apulia Carbonate Platform. Thus, the porosity value adopted for resolving the Eq. (6) is $\phi = 0.45$, corresponding to that typical for this residual sediment (Walsh, personal communication). Diffusion coefficients are tabulated for species in aqueous solution and that for Al^{3+} is $D = 0.57 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Ly and Gregory, 1975). However, diffusion through a sediment is slower due to the combined effect of porosity and tortuosity and the diffusion coefficient, as a good approximation, can be obtained as follows (cf. Drever, 1997):

$$D_{\text{sediment}} = \frac{D_{\text{solution}}}{\phi^{-2}} \quad (6)$$

Thus, the calculated diffusion coefficient of Al^{3+} in the matrix of the bauxite is $0.12 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

The differences in the equilibrium concentrations of Al^{3+} ions at the surface of dissolving kaolinite and alternatively precipitating Al-hematite and boehmite, are calculated using the solubility product constants of kaolinite and Al-hematite and boehmite proposed by Tardy and Nahon (1985) for bauxites and ferricretes. The congruent dissolution of kaolinite and its solubility product are:



$$K_{\text{sp}} = \frac{a_{\text{Al}^{3+}}^3 a_{\text{SiO}_{2(\text{aq})}}^2 a_{\text{H}_2\text{O}}^5}{a_{\text{H}^+}^6} = 7.410 \quad (8)$$

The Al-hematite can be considered as a solid solution between hematite and corundum with a formula $(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_3$, where x is the molar fraction of Al_2O_3 involved in the solid solution (Tardy and Nahon, 1985). The congruent dissolution of the corundum and the corresponding solubility product, assuming the solid solution exhibits ideal behavior, are:



$$K_{\text{sp}} = \frac{a_{\text{Al}^{3+}}^2 a_{\text{H}_2\text{O}}^3}{x_{\text{Al}_2\text{O}_3} a_{\text{H}^+}^6} = 19.266 \quad (10)$$

The Al-hematite precipitates in a water-unsaturated environment and the value of the water activity may be fixed at 0.5. a_{H^+} is supposed to be 10^{-7} because maximum hematite precipitation occurs at near neutral pH (Schwertmann and Murad, 1983). If quartz controls silica activity, the $a_{\text{SiO}_{2(\text{aq})}}$ is 10^{-4} . The molar fraction of Al_2O_3 in Al-hematite, as

previously stated, is 0.12. The difference in the equilibrium concentrations of Al^{3+} ions at the surface of dissolving kaolinite and precipitating Al-hematite is $c_d - c_p = 1.5398 \times 10^{-13}$ m/g. Finally, the estimated average volume fraction of Al-hematite in the concretions is 0.6 whereas the kaolinite volume fraction in the bauxite matrix is 0.4. On this basis is ≈ 180 ka the time required to grow a core having an average radius of $31.4 \mu\text{m}$ whereas the accretionary band having a radius of $5.4 \mu\text{m}$ grows in ≈ 8 ka.

If water activity decreases boehmite instead of Al-hematite forms at the expense of kaolinite. The congruent dissolution of boehmite and its solubility product are:



$$K_{\text{sp}} = \frac{a_{\text{Al}^{3+}} a_{\text{H}_2\text{O}}^2}{a_{\text{H}^+}^3} = 8.345 \quad (12)$$

Assuming arbitrarily 0.2 as the value of water activity the difference in the equilibrium concentrations of Al^{3+} ions at the surface of dissolving kaolinite and precipitating boehmite is $c_d - c_p = 1.5395 \times 10^{-13}$ m/g. The estimated average volume fraction of boehmite in the concretions is 0.2. The time required to grow a boehmite accretionary band with a radius of $5.1 \mu\text{m}$ is ≈ 4.5 ka.

Finally, because the number of alternating accretionary bands is within the range 20–30, the time required to form the core is comparable to that necessary for the growth of the cortex (125–190 ka), whereas the average bulk concretions possibly formed in 300–400 ka.

4. Conclusion

The mineralogical and chemical features of bauxites strictly reflect environmental constraints (Tardy et al., 1990, 1991; D'Argenio and Mindszenty, 1995; Tardy and Roquin, 1998). Beauvais (1999) suggests that ferrugination producing nodular ferricrete is not a simple ongoing process but may result from different stages of weathering during climatic changes. The formation of the concretions, which are a late product of the “in situ” bauxitization of the clay accumulated in the karst, is a two-stage process likely resulting from climatic changes. In the first stage, a large Al-hematite core formed resulting from a relatively long period of dominantly wet tropical climate: the pedogenic environment did not allow for the weathering system to be water-saturated but the rainfall regime likely did not permit drier conditions. In the second stage, time-limited drier conditions, possibly related to eustatic sea-level drops and favouring boehmite stability alternated with a time-limited wetter climate favouring Al-hematite stability. This climatic alternation is in agreement with the assumption that in the Phanerozoic history the Mesozoic represents the longest period of warmth punctuated by oscillations in climate (Price, 1999). The importance of both climatic and eustatic controls for carbonate platform succession of the southern Apennines during the Cretaceous age has been well established using microstratigraphic analysis (D'Argenio et al., 1997; Buonocunto et al., 1999). Buonocunto et al. (1999) also suggested these controls are related mostly to the Earth's orbital

periodicities which in the upper Cretaceous produce elementary cycles representing the cycle of the equinoxes (≈ 20 ka), the short eccentricity cycle (≈ 100 ka), and the long eccentricity cycle (≈ 400 ka). These cyclic component are common in the worldwide sedimentary record (e.g. Berger, 1988). The calculated time requiring the whole concretion to form (300–400 ka) is consistent with the long eccentricity cycle, whereas the short time cycles are not applicable to the apulian karst bauxite concretions. This is possibly due to local factors including tectonic discontinuities (Luperto Sinni et al., 1991) which produced appreciable perturbations on weathering processes (e.g. Nahon, 1991) and especially to those related to a short period cyclicity.

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